Inorganica Chimica Acta, 140 (1987) 93–95

Synthesis, Crystal Structure and Magnetic Properties of New Ternary Uranium Chalcogenides: $RuUS_3$ and $RhUS_3$*

A. DAOUDI and H. NOEL†

Université de Rennes 1, Laboratoire de Chimie Minerale B, Chimie du Solide et Inorganique Moléculaire, U.A. 254 C.N.R.S., Avenue du Général Leclerc, 35042 Rennes, France

A large number of ternary uranium and 3d transition metal chalcogenides have been reported; they correspond to three formulae, MUX_3, MU_2X_5 and MU_8X_{17} (M = 3d metal, X = S, Se) and crystallize with four crystal structure types [1–3]. We have investigated other M–U–X ternary systems with M = 4d and 5d transition metals, and with M = Pd; compounds of formulae UPd_2S_4, UPd_3S_4, PdU_2X_4 and $PdUSe_3$ have been characterized [4–7]. We report here part of our investigations with rhodium and ruthenium, *i.e.* the new compounds $RuUS_3$ and $RhUS_3$.

Synthesis and Characterization

$RuUS_3$ and $RhUS_3$ were prepared by heating stoichiometric mixtures of sulfur, uranium disulfide, and rhodium or ruthenium, in sealed silica tubes at high temperature ($T \geq 1150$ °C) for one day. Single crystals of $RhUS_3$ could be obtained by the gas phase transport method, using iodine as transporting agent and a temperature gradient of 1000–930 °C. Single crystals of $RuUS_3$ could not be obtained.

The X-ray powder diffraction patterns suggested these compounds to be isotypic with $CrUS_3$ [1], which crystallizes in the orthorhombic system, space group *Pnam*. The lattice parameters obtained from least-squares refinement of the X-ray powder data are: $RuUS_3$, $a = 6.939(2)$ Å, $b = 5.896(2)$ Å, $c = 8.770(3)$ Å, $V = 359$ Å^3; $RhUS_3$, $a = 7.119(2)$ Å, $b = 5.978(2)$ Å, $c = 8.618(2)$ Å, $V = 367$ Å^3.

Crystal Structure of $RhUS_3$

A crystal with dimensions 0.13 × 0.11 × 0.11 mm was used for the crystal structure determination. X-ray diffraction intensities were collected in the range $1 < \theta < 35$ with the ω–2θ scan method on a Nonius Cad4 four-circle diffractometer, with Mo Kα radiation. The number of unique reflections measured was 965, and 708 intensities such as $I > 3\sigma(I)$ were considered as observed and corrected for absorption on assimilating the crystal to a sphere, with $\mu r = 2.6$. All calculations and full matrix least-squares refinements were made using the SDP program system [8]. Uranium, rhodium and sulfur atoms were located as with $CrUS_3$ in the 4c, 4a, 4c and 8d positions of the *Pnam* space group. Refinements of positional and isotropic thermal parameters led to $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o| = 0.061$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.092$, which were reduced to $R = 0.033$ and $R_w = 0.054$ when anisotropic thermal factors were introduced. The positional and thermal parameters are given in Table I and the main interatomic distances in Table II.

Figure 1 shows a projection of the structure down the *b* axis. The uranium environment is a bicapped trigonal prism, with a mean uranium to sulfur

TABLE I. Atomic Parameters for $RhUS_3$[a]

	U	Rh	S(1)	S(2)
Site	4c	4a	4c	8d
x	0.38191(5)	0.0	0.0494(5)	0.3204(3)
y	0.06386(7)	0.0	0.8513(6)	0.8431(3)
z	0.25	0.0	0.25	0.5524(2)
β_{11}	0.61(1)	0.97(3)	1.44(9)	0.84(6)
β_{22}	1.28(1)	1.05(2)	1.5(1)	0.71(5)
β_{33}	0.88(1)	1.01(3)	0.93(9)	0.93(6)
β_{12}	0.19(1)	−0.05(2)	−0.68(8)	−0.12(4)
β_{13}	0	−0.07(2)	0	−0.05(5)
β_{23}	0	−0.05(3)	0	0.00(5)
B_{eq}	0.922(6)	1.01(1)	1.28(5)	0.83(3)

[a] Standard deviations are in parentheses.

---

*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

†Author to whom correspondence should be addressed.

0020-1693/87/$3.50

TABLE II. Interatomic Distances for RhUS$_3$^{a} (Å)

U–S(1)	2.687(3)	Rh–2S(1)	2.353(1)
S(1)	2.757(3)	2S(2)	2.461(2)
2S(2)	2.773(2)	2S(2)	2.508(2)
2S(2)	2.785(2)	2U	3.485(0)
2S(2)	2.950(2)	2U	3.487(0)
2Rh	3.485(0)	2Rh	4.300(0)
2Rh	3.487(0)		
2U	4.199(0)		
S(1)–2Rh	2.353(1)	S(2)–Rh	2.461(2)
U	2.687(3)	Rh	2.508(2)
U	2.757(3)	U	2.773(2)
2S(2)	3.238(3)	U	2.785(2)
2S(2)	3.282(3)	U	2.950(2)
2S(2)	3.523(3)	S(1)	3.238(3)
2S(2)	3.606(3)	S(1)	3.282(3)
2S(2)	3.628(3)	2S(2)	3.283(2)
U	3.699(3)	S(2)	3.298(3)
2S(1)	3.760(2)	S(2)	3.399(4)
		S(1)	3.523(3)
		S(1)	3.606(3)
		S(1)	3.628(3)
		2S(2)	3.729(1)

^{a}Standard deviations in parentheses.

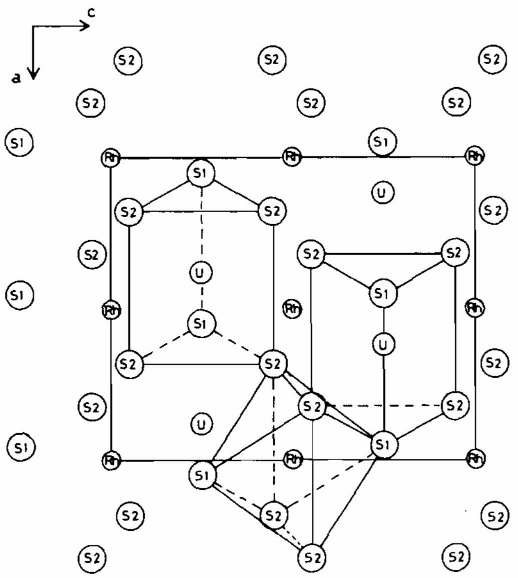

Fig. 1. Projection of the crystal structure in the (*a*,*c*) plane.

distance equal to 2.81 Å, which indicates uranium to be in a tetravalent state [9]. Rhodium has a distorted octahedral environment: this element is generally trivalent in its chalcogenides but the mean distance Rh–S = 2.44 Å is higher than the usual distance Rh^{3+}–S = 2.35–2.36 Å in octahedral coordination [10, 11]. A trivalent state for rhodium would imply an electron delocalization according to the simple ionic valence scheme: Rh^{3+}U^{4+}S$_3$$^{2-}$ + e$^-$; the available single crystals were not of suitable size to give evidence for this delocalization by resistivity measurements.

Magnetic Properties

The magnetic properties of RuUS$_3$ and RhUS$_3$ were investigated using a SQUID magnetometer. In the paramagnetic region, the thermal variations of the reverse susceptibilities of the two compounds (Fig. 2) showed some curvature towards the temperature axis, and were fitted according to the modified Curie–Weiss law: $X = X_0 + C/(T - \theta)$: the existence of significant temperature independent

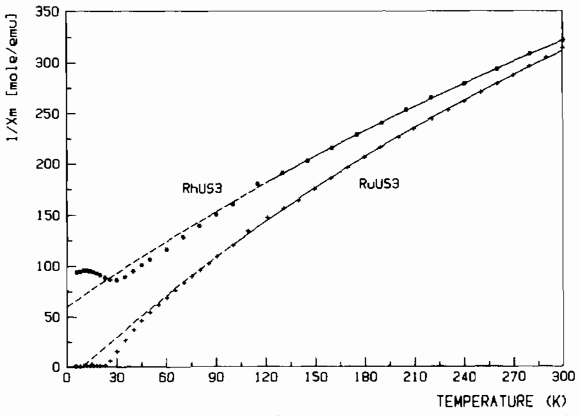

Fig. 2. Thermal variation of the reverse magnetic susceptibility of RhUS$_3$ and RuUS$_3$.

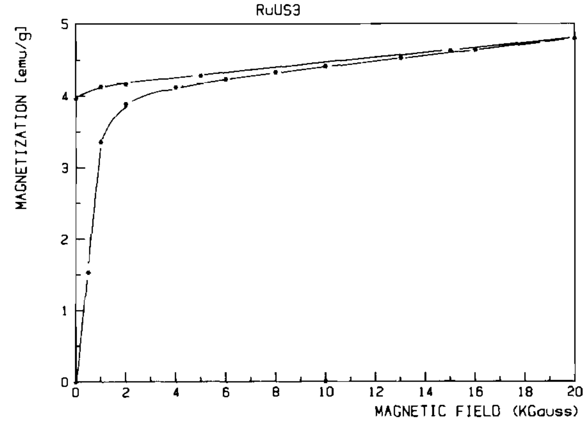

Fig. 3. Magnetization curve at $T = 5$ K for $RuUS_3$.

terms X_0 suggesting the presence of conduction electrons. The paramagnetic constants for the two compounds are: $RuUS_3$, $C = 0.666$, $\mu_{eff} = 2.31$ μ_B, $\theta = 10$ K, $X_0 = 923 \times 10^{-6}$ emu mol^{-1}; $RhUS_3$, $C = 0.80$, $\mu_{eff} = 2.53$ μ_B, $\theta = -51$ K, $X_0 = 826 \times 10^{-6}$ emu mol^{-1}. In both cases, the effective magnetic moment has rather low values for uranium in the tetravalent state. Although they do not contribute to the paramagnetic moment, the 4d transition elements have large influence on the low temperature behavior: The reverse susceptibility of $RhUS_3$ shows a minimum suggestive of antiferromagnetic ordering of the uranium moments at $T_N = 30$ K; $RuUS_3$ orders ferromagnetically at $T_c = 26$ K, in agreement with the respective signs of the paramagnetic Curie constants. Figure 3 shows the magnetization curve for $RuUS_3$ at $T = 5$ K; the value of the ordered magnetic moment, 0.31 μ_B/U, is close to that found in $CrUS_3$ [12], and may result from a canted magnetic structure of the uranium moment.

References

1 H. Noel, J. Padiou and J. Prigent, *C. R. Acad. Sci. C, 272*, 206 (1971).
2 H. Noel, M. Potel and J. Padiou, *Acta Crystallogr., Sect. B, 32*, 605 (1976).
3 H. Noel, M. Potel and J. Padiou, *Acta Crystallogr., Sect. B, 31*, 2634 (1975).
4 A. Daoudi and H. Noel, *J. Solid State Chem., 60*, 131 (1985).
5 A. Daoudi and H. Noel, *Inorg. Chim. Acta, 117*, 183 (1986).
6 A. Daoudi and H. Noel, *J. Less-Common Met., 115*, 253 (1986).
7 A. Daoudi and H. Noel, to be published.
8 B. A. Frenz, in H. Schenk, R. Olthof-Hazekemp, H. V. Koningsveld and G. Bassi (eds.), 'Computing in Crystallography', Delft University Press, Delft, 1978.
9 H. Noel, *J. Solid State Chem., 52*, 203 (1984).
10 E. Parthé, D. Hohnke and F. Hulliger, *Acta Crystallogr., 23*, 832 (1967).
11 Y. Tretyakov, I. V. Gordev and Y. A. Kesler, *J. Solid State Chem., 20*, 345, 1977.
12 P. Wolfers, G. Fillion, M. Bacman and H. Noel, *J. Phys., 37*, 233 (1976).